A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the IIT NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.
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Deadline Dates:  No. 108: 8 September 1967
No. 109: 7 October 1967

Reminder: For the period August 10, 1967 to August 15, 1968 inclusive, all Newsletter contributions, enquiries, etc., should be addressed as follows:

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

- continued on outside back cover
1. Policy: The IIT NMR Newsletter is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything." (This is usually followed by the mental reservation "that won't land us in jail"). Virtually no editorial functions are performed, but the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, etc., should not be considered adequate. The IIT NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in.

As suitable subjects for contributions, we have suggested the following:

1. Reproductions of particularly interesting spectra or parts of spectra.
2. Measurements and calculations of same.
3. Theoretical considerations and interpretations.
5. Complete or partial mysteries.
6. Comments on material appearing in earlier letters.
7. Requests for help in locating odd or rare compounds.
8. Announcements of forthcoming meetings, colloquia, symposia, books, etc. Also "Preprints Available".
9. Notices of "Positions Available" or "Situations Wanted". We will be happy to include such notices along with any more substantive contribution.
10. Wild theories (this category added at the request of Dr. Ray Freeman).
11. Anything else which you feel your co-workers in the field might find interesting - even mild polemics.

Foreign participants should not feel obliged to render their contributions in English.

2. Bibliography: The titles and references appearing in the "Bibliography" section are those which the NMR people at Mellon Institute come across in their perusal of the literature. No claims for completeness are made and we once again invite all participants to send in references and titles which we have missed for inclusion in a subsequent issue. This invitation is extended particularly to foreign, and most especially foreign-language, journals, since this is where the NMR searching is most apt to be late at best and also incomplete at worst.

Since there appears to be no simple, objective way of deciding on the inclusion of some NMR-containing references and the exclusion of others, the Bibliography will continue to list (in alphabetical order of journal name) all references found which contain any NMR data, spectra or other "hard" information. The Bibliography is printed on only one side of the page, so each reader can take scissors in hand and do his own custom editing.

3. Subscriptions: We will continue to send out the IIT NMR Newsletter without charge although we would be grateful for the cooperation of all participants as outlined in the section below on "Practical Considerations". We are willing to send your issue by air-mail if you are willing to pay the rather formidable air-mail postage; rates and ground rules on request.

Participation is the prime requisite for receiving the IIT NMR Newsletter; in order to receive the Newsletter, you must make at least occasional contributions to its content. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution, you will receive a "reminder letter". If no contribution is then forthcoming ten months after your last contribution, you will receive the "ultimatum letter", and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending in a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of 9 per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

PLEASE NOTE: A subject of considerable interest and concern to several present and potential IIT NMR Newsletter participants - as well as to ourselves - is whether the IIT NMR Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it
would appear in the Newsletter. Our attitude is that an IIT NMR Newsletter contribution should not
duplicate, summarize or abstract material which has been published or which will appear in the formal
literature within a small number of weeks of the IIT NMR Newsletter account. On the other hand, let it
be firmly emphasized that if the appearance in a journal is several months away - as is frequently the
case - a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal
account, a selection of material from the manuscript, or what have you) sent in to the IIT NMR Newsletter
fulfills one of the very functions which we feel this Newsletter can provide. We trust that a partici-
panent will in each case himself apply the criterion of whether or not his contribution will communicate
some subject matter to the IIT NMR Newsletter audience before they could read it elsewhere.

4. Public Quotation: Public quotation of Newsletter contents in print or in a talk is
expressly forbidden (except as follows), and reference to the IIT NMR Newsletter by name in the scientific
literature is never permissible. We remind you that in order to quote results or use material from the
IIT NMR Newsletter it is necessary, in each individual case, to obtain the prior permission of the author
in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the
actual recipient of the Newsletter to see that these other readers of your copy are acquainted with and
abide by the statements of policy and practical considerations.

5. Practical Considerations: (a) All contributions to the IIT NMR Newsletter should be sent
to the undersigned and will alway be included in the next issue if received before the deadline dates,
which appear on the cover of each issue.

(b) Contributions should be on the minimum (NOTE!!) number of 8-1/2 x 11" (21 x 27.5 cm)
pages, printed on one side only, with at least 3/4" (2 cm) margins on all sides. Black ink, typing,
drawings, etc., on white paper are good; grey or blue ink, typing, etc., on anything are ghastly - i.e.,
high contrast is essential. We are not equipped to deal with large size pieces of paper - e.g. A-50 charts.

Please conserve space by avoiding double spacing except where necessary, ultra-wide margins,
self-filled pages, etc. In general, please plan and construct your contribution so as to fill the
minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility
when they are too small. However, it should rarely, if ever, be necessary for a contribution to exceed
4 pages in length, including figures.

Since reproductions of various kinds do not themselves reproduce too well, contributors are
urged to submit their photographic originals to us (if the size does not exceed 8-1/2 x 11"), and we will
be happy to return these if requested. Some law of physics says that photographic reproductions of fuzzy
or blurred originalas never come out less fuzzy or blurred.

(c) Please provide short titles of all the topics of your contributions, as this will
ensure accuracy in preparing the title-page index.

(d) Please do not send in manuscripts, theses, books, etc., and ask us to be your consciences
in selecting what should and shouldn't go into the Newsletter

6. Suggestions: They are always welcome.

B. L. Shapiro
26 July 1967

Associate Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

* Temporary address for the period 10 August '67 to 15 August '68:
Department of Chemistry, Stanford University, Stanford, California 94305.
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

The PLOT program of Swalen and Reilly has been incorporated as a subroutine in NMRIT. This was a cooperative project with FDA; Jim Ferretti carried out the necessary revisions. Plotting parameters are included on an extra NMRIT data input card; the PLOT call is optional. The program is for a CDC 3800, and 65K of memory are necessary. Eventually, we hope to reduce the storage requirements considerably. Fortran listings are available.

Our continuing interest in $^{14}$N NMR of aliphatic nitro compounds prompts us to ask IITNMRN readers for donations of 0.5g samples of uncommon members of this class of compounds. In return, we can offer $^{14}$N spectra of compounds having reasonable line widths.

Hoping that the above will keep the humbugs away, I venture to point out that the NRL postdoctoral positions mentioned in IITNMRN 98-19 are available each year.

Sincerely,

W. B. McNiz, Head  
NMR Spectroscopy Section  
Chemistry Division

TITLE: NMRIT with PLOT,  
Aliphatic Nitro Compounds Solicited,  
Postdoctoral Positions.
Title: Long range couplings in 1,3-dioxolan-4-ones

Dear Professor Shapiro,

We have observed long range couplings in the three 1,3-dioxolan-4-ones A (Chloralide), B, and C.

For A the coupling constant is 1.5 cps \(^1\). B and C show highly stereospecific couplings, one being of about the same magnitude as in A, the other considerably smaller. For B an ABX analysis at 60 and 100 Mc yielded the same sign for the two long range couplings in all solvents; spin tickling experiments in CD\(_3\)CN and (CD\(_3\))\(_2\)CO gave positive signs for the two couplings (negative sign assumed for the geminal coupling constant). We therefore feel justified to assign positive values to all the long range couplings observed in these compounds. We determined the (hitherto unknown) stereochemistry of Chloralide (A) by dipole moment measurements of the compounds A, B and C. The results clearly show that the CCl\(_3\) groups...
Table I: NMR parameters of 2,5-bis(trichloromethyl)-1,3-dioxolan-4-one (A)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_A$ (ppm)</th>
<th>$\tau_X$ (ppm)</th>
<th>$J_{AX}$ (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-$d_6$</td>
<td>5.49</td>
<td>4.62</td>
<td>1.50</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.09</td>
<td>4.13</td>
<td>1.50</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>4.97</td>
<td>4.00</td>
<td>1.50</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>4.87</td>
<td>3.93</td>
<td>1.50</td>
</tr>
<tr>
<td>CD$_3$ CN</td>
<td>4.48</td>
<td>3.63</td>
<td>1.50</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ CO</td>
<td>4.24</td>
<td>3.43</td>
<td>1.50</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ SO</td>
<td>3.80</td>
<td>3.11</td>
<td>1.50</td>
</tr>
<tr>
<td>Pyridine-$d_5$</td>
<td>3.6</td>
<td>3.08</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Table II: NMR parameters of 2-(trichloromethyl)-1,3-dioxolan-4-one (B)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_A$</th>
<th>$\tau_B$</th>
<th>$\tau_X$</th>
<th>$J_{AX}$</th>
<th>$J_{BX}$</th>
<th>$J_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-$d_6$</td>
<td>6.20</td>
<td>6.54</td>
<td>4.80</td>
<td>1.45</td>
<td>0.15</td>
<td>-15.05</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.58</td>
<td>5.77</td>
<td>4.30</td>
<td>1.35</td>
<td>0.10</td>
<td>-14.80</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>5.50</td>
<td>5.65</td>
<td>4.21</td>
<td>1.50</td>
<td>0.15</td>
<td>-14.85</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>5.44</td>
<td>5.60</td>
<td>4.19</td>
<td>1.40</td>
<td>0.10</td>
<td>-14.90</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>5.37</td>
<td>5.54</td>
<td>4.11</td>
<td>1.50</td>
<td>0.15</td>
<td>-15.20</td>
</tr>
<tr>
<td>CD$_3$ CN</td>
<td>5.38</td>
<td>5.48</td>
<td>3.97</td>
<td>1.50</td>
<td>0.25</td>
<td>-15.40</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ CO</td>
<td>5.31</td>
<td>5.37</td>
<td>3.84</td>
<td>1.50</td>
<td>0.25</td>
<td>-15.10</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ SO</td>
<td>5.25</td>
<td>5.29</td>
<td>3.67</td>
<td>1.40</td>
<td>0.35</td>
<td>-15.40</td>
</tr>
</tbody>
</table>

Table III: NMR parameters of 5-trichloromethyl-1,3-dioxolan-4-one (C)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_A$</th>
<th>$\tau_M$</th>
<th>$\tau_X$</th>
<th>$J_{AX}$</th>
<th>$J_{MX}$</th>
<th>$J_{AM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-$d_6$</td>
<td>5.10</td>
<td>5.39</td>
<td>5.91</td>
<td>1.40</td>
<td>0.30</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>4.24</td>
<td>4.39</td>
<td>5.30</td>
<td>1.50</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>4.21</td>
<td>4.38</td>
<td>5.20</td>
<td>1.50</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>CD$_3$ CN</td>
<td>4.26</td>
<td>4.38</td>
<td>5.01</td>
<td>1.40</td>
<td>0.40</td>
<td>0.20</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ CO</td>
<td>4.18</td>
<td>4.28</td>
<td>4.86</td>
<td>1.30</td>
<td>0.40</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>(CD$_3$)$_2$ SO</td>
<td>4.21</td>
<td>4.32</td>
<td>4.62</td>
<td>1.20</td>
<td>0.55</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>
Table IV: NMR parameters of 2,5-bis(trichloromethyl)-3-methyl-oxazolidin-4-one (D)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_A$</th>
<th>$\tau_X$</th>
<th>$J_{CH_2}$</th>
<th>$J_{AX}$</th>
<th>$J_{A-CH_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-d$_6$</td>
<td>5.28</td>
<td>5.16</td>
<td>7.40</td>
<td>2.15</td>
<td>0.40</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>5.11</td>
<td>4.52</td>
<td>6.80</td>
<td>2.20</td>
<td>0.40</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>5.00</td>
<td>4.46</td>
<td>6.77</td>
<td>2.30</td>
<td>0.45</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>4.82</td>
<td>4.23</td>
<td>6.83</td>
<td>2.10</td>
<td>0.45</td>
</tr>
<tr>
<td>(CD$_3$)$_2$CO</td>
<td>4.73</td>
<td>4.04</td>
<td>6.76</td>
<td>2.15</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table V: Dipole moments of the 1,3-dioxolan-4-ones A, B and C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Compound</th>
<th>$\mu$ exp.(D)</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>B</td>
<td>2.27</td>
<td>2.31</td>
<td>2.34</td>
<td>2.87</td>
</tr>
<tr>
<td>Benzene</td>
<td>B</td>
<td>2.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C</td>
<td>2.94</td>
<td>2.92</td>
<td>3.34</td>
<td>3.57</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>A (trans)</td>
<td>1.80</td>
<td>1.56</td>
<td>1.07</td>
<td>2.46a)</td>
</tr>
<tr>
<td>Benzene</td>
<td>A (trans)</td>
<td>1.53</td>
<td></td>
<td></td>
<td>1.44b)</td>
</tr>
<tr>
<td></td>
<td>A (cis)</td>
<td></td>
<td>3.47</td>
<td>3.11</td>
<td>3.51</td>
</tr>
</tbody>
</table>

a) 2-CCl$_3$ axial, 5-CCl$_3$ equatorial
b) 2-CCl$_3$ equatorial, 5-CCl$_3$ axial

* I: planar ring
II: $O_1$, C$_5$, C$_4$ and O$_3$ in one plane, C$_2$ 0.6 Å out of plane
III: C$_2$, O$_3$, C$_4$ and C$_5$ in one plane, O$_1$ 0.6 Å out of plane

Bond distances and approximate angles from:
The crystal structure of D-galacton-\(\gamma\)-lactone,
G.A. Jeffrey, R.D. Rosenstein and M. Vlasse,
Acta Cryst. 22, 725 (1967)

Group dipole moments from:
C.P. Smyth,
Dielectric Behaviour and Structure
in Chloralide are trans, and consequently the large coupling occurs between transsituated protons. This result practically excludes a four bond mechanism because of the very unfavourable stereochemistry for such a coupling. We therefore assume that the coupling occurs via five bonds by $\sigma$-$\pi$ interaction, analogous to homoallylic coupling\(^2\).

Strong support for this assumption is given by the spectra of the oxazolidin-4-one D. In this compound the cross ring coupling is considerably larger than in A (2.1 - 2.3 cps), presumably because of the higher partial double bond character of the $\text{C}-\text{N}$ bond as compared to the $\text{C}-\text{O}$ bond. Furthermore a five bond coupling between one ring proton and the $\text{N-CH}_3$ group of about .4 cps is observed\(^3\).

Quite unexpectedly, we found no appreciable coupling in the lactone E. The signals for the $\text{CH}_2$ groups of this compound are singlets at $\tau = 6.04$ and $\tau = 7.68$, with halfwidths of .55 cps.

NMR parameters for compounds A - D in various solvents are given in Tables I - IV. The spectra were measured at 60 and 100 Mc on Varian A-60 and HA-100 instruments. Concentrations were approximately 10% w/v.

Measured dipole moments for A, B, and C together with values calculated for three conformations of the rings are given in Table V. The experimental values are estimated to be accurate to .05 Debye units.

A detailed discussion of the results on these and related compounds will be published elsewhere.

Yours sincerely,

[Signature]

1.) This coupling has already been reported by M. Baron and D.P. Hollis, Rec. Trav. Chim. 84, 1109 (1965).

2.) Small couplings ($\sim .2$ cps) of this type in carboxylic esters have recently been reported by K. Hayamizu and O. Yamamoto, J.Mol.Spectr. 22, 119 (1967).

3.) For Dimethylacetamide a coupling of .5 cps between the trans $\text{CH}_2$ groups was observed by R.C. Neumann and L. Brewster Young, J.Phys.Chem. 69, 1777 (1965).
Although there has been quite a lot written about the effect of rapid conformational interconversion on NMR spectra, I feel that there is still a need for some simple rules to enable the spectroscopist to predict the type of spectrum to be expected for any given molecule. The following rules formulated by Jack Mortimer have a firm basis in group theory and, I believe, are useful ones for this purpose.

There are two classes of nuclei: I and II.

Class I Nuclei:

These are nuclei in a group of atoms containing an axis of C2, or higher, symmetry coincident with the bond connecting the group to the rest of the molecule. Nuclei that are permuted by rotation about this symmetry axis are magnetically equivalent and will remain so under rapid reorientation about the symmetry axis regardless of the symmetry of the molecule as a whole. This means that such nuclei will have the same chemical shift and the same coupling constant to any other set of equivalent nuclei.

Examples:

\[ C_2: \quad -\text{CH}_3, \quad -\text{CF}_3, \quad -\text{C(CH}_3)_3; \]

\[ C_3: \quad \text{H}_X \text{Y} \]

Dr. Jack Mortimer
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry,

I am writing to you in response to your current study of the rapid conformational interconversion of the diacetylene compound described in your recent publication. My colleague, Dr. John Shapiro, and I have been engaged in similar studies and have found that the effect of rapid conformational interconversion on the NMR spectra can be predicted using a set of simple rules.

These rules, formulated by Jack Mortimer, are based on group theory and provide a useful tool for predicting the NMR spectra of molecules that undergo rapid conformational interconversion. The rules can be summarized as follows:

Class I Nuclei:

These are nuclei in a group of atoms containing an axis of C2, or higher, symmetry coincident with the bond connecting the group to the rest of the molecule. Nuclei that are permuted by rotation about this symmetry axis are magnetically equivalent and will remain so under rapid reorientation about the symmetry axis regardless of the symmetry of the molecule as a whole. This means that such nuclei will have the same chemical shift and the same coupling constant to any other set of equivalent nuclei.

Examples:

- \( C_2: \quad -\text{CH}_3, \quad -\text{CF}_3, \quad -\text{C(CH}_3)_3; \)

- \( C_3: \quad \text{H}_X \text{Y} \)

I hope this information is helpful. Please let me know if you have any further questions.

Sincerely,

[Signature]
Class II Nuclei.

All nuclei not in Class I are in Class II.

To determine the kind of NMR spectrum:

1. Place the molecule in the conformation of highest symmetry (not necessarily the one of lowest energy). A model will help.

2. Nuclei that are symmetrically equivalent under the symmetry operations applicable to this conformation will have the same chemical shift under conditions of rapid reorientation through all possible conformations.

3. The number of distinct coupling constants to be expected under conditions of rapid reorientation will be the same as the number of such constants expected for the conformation of highest symmetry. (In some cases a very high quality spectrum may be needed to detect differences in values of constants.)

Examples of Class II Nuclei:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Highest Symmetry</th>
<th>Spectral Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CHXY-CH2Z</td>
<td>None</td>
<td>ABC</td>
</tr>
<tr>
<td>2. CH2X-CH2Z</td>
<td>C2</td>
<td>AA'B'B'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(A2B2 approx.)</td>
</tr>
<tr>
<td>3. CHXY-CH2-CHXY</td>
<td>C2</td>
<td>AA'C2</td>
</tr>
<tr>
<td>a) Optically Active</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Meso</td>
<td>C2</td>
<td></td>
</tr>
<tr>
<td>4. CHXY-CHZ-CHXY</td>
<td>C2</td>
<td>ABC</td>
</tr>
<tr>
<td>a) Optically Active</td>
<td>None</td>
<td>ABC</td>
</tr>
<tr>
<td>b) Meso</td>
<td>C2</td>
<td>AC2</td>
</tr>
<tr>
<td>5. CHXY-CH2-CH2-CHXY</td>
<td>C2</td>
<td>AA'B'B'C'C'</td>
</tr>
<tr>
<td>a) Optically Active</td>
<td></td>
<td>(AA'B'B'C2 approx.)</td>
</tr>
<tr>
<td>b) Meso</td>
<td>C2</td>
<td>AA'B'B'C'C'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(AA'B'B'C2 approx.)</td>
</tr>
</tbody>
</table>
Dr. B. L. Shapiro

July 13, 1967

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Highest Symmetry</th>
<th>Spectral Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. ((\text{CH}_3\text{O})_2\text{P})</td>
<td>(\text{Cs})</td>
<td>(A_6X)</td>
</tr>
<tr>
<td>7. ((\text{CH}_3\text{O})_2\text{P}-\text{CH}<em>2\text{-P(OC}</em>\text{H}_3\text{)}_2)</td>
<td>(\text{Cs})</td>
<td>(A_3A_3'B_3B_3'XX')</td>
</tr>
<tr>
<td>8. ((\text{CH}_3\text{CH}_2\text{O})_2\text{S}=\text{O})</td>
<td>None</td>
<td>(A_3A_3'C_2D_2)</td>
</tr>
</tbody>
</table>

Sincerely yours,

Charlie

C. A. Reilly

CAR: jel
Subject: NMR of Iminoxy1 Radicals.

Dear Professor Shapiro,

In our letter we want to say few words about the current NMR research of free radicals in our Institute.

As it has been shown by Hauser et al. the NMR method may be successfully applied for the investigation of the hyperfine interactions in free radicals. This method allows direct determination both magnitude and signs of the coupling constant $\alpha_i$. We have studied the NMR-spectra of the number of iminoyl radicals synthesized by E.G. Rozantzev. The optimum conditions for the spectra recording have been found. The line widths have a minimum on the concentration of a radical and they are decreased as the temperature increases. All the spectra had several lines according to the number of the equivalent protons group. The proton resonance spectrum of the 2,2,6,6-tetramethylpiperidin-1-oxyl at 100 Mc/sec. is shown in fig.1. The hyperfine interactions constants, calculated from the paramagnetic shifts, are shown in the same fig.1.

The examination of the data for the different radicals demonstrates the sensitivity of the coupling constants to their geometry. The constants $\alpha_i$ on the $\gamma$-hydrogens (with respect to the nitrogen atom) have the negative sign. This indicates an essential contribution of the mechanism of the spin polarization in the spin density propagation. The spin density on the $\delta$-hydrogen have the positive sign unlike $\gamma$-hydrogen.
Consideration of the possible mechanisms of the spin density propagation through \( \sigma \)-bonds and the influence of geometry of radicals on the coupling constant with \( \gamma \)-protons are now in progress.

We look forward to the continued receipt of your valuable and interesting newsletter.

Sincerely yours

Yu. Molin

R. Sagdeev

V. V. Voevodsky

---

THE INSTITUTE OF THE CHEMICAL KINETICS AND COMBUSTION WITH GREAT SORROW INFORMS YOU OF THE Sudden death of vice-director, Academician, Professor

V. V. Voevodsky

Colleagues, friends
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Ill. 60616

Dear Barry:

Aromatic Proton Chemical Shifts in Meisenheimer Complexes of Nitroarenes.

In response to your ever so gentle stimulus, I should like to report the results of some recent studies of the spectra of Meisenheimer complexes; these studies have been carried out in collaboration with W. E. Byrne, E. J. Fendler and J. H. Fendler. Treatment of both 2,4-dinitrophenyl and -naphthyl alkyl ethers with potassium alkoxides results in the formation of the crystalline complexes I and II. The stability of these complexes are sufficiently great so that good spectra can be obtained in DMSO-d$_6$.

The spectra of these complexes are fully consistent with the postulated structures; other studies of the spectra of Meisenheimer complexes generated in situ have been reported by Servis* and Foster and Fyfe**. Based on our results to date, it appears that the chemical shifts of the aromatic protons in these complexes reflect the relative charge densities at the ring positions in a fairly sensitive fashion. Although the major portion of the negative charge is accomodated by the nitro groups, appreciable shielding effects are observed for the ring protons. Thus, for the phenyl complexes (I), all three protons are shielded relative to the corresponding protons in the parent ether (positive $\Delta\delta$ values indicate upfield shifts). The only position at which negative charge can be localized by conventional canonical structures is H-6 and, as expected, this proton undergoes the greatest upfield shift.

The magnitudes of the observed $\Delta\delta$ values for the naphthyl complexes (***.) are smaller; this attenuation is anticipated since the negative charge is delocalized over a much larger system. Protons-3, -6 and -7 undergo the expected upfield shifts but H-3 and H-8 are deshielded to a lesser, but real, degree. This downfield shift was unexpected, but, after the completion of these studies, a report*** of HMO calculations of charge densities in these complexes appeared. These calculations are in semi-quantitative agreement with the observed $\Delta\delta$ values; the reduction in electron density at H-3 in II and the relative electron densities at the three positions of I are in particularly good agreement.
We are continuing with studies of the spectra of these complexes, particularly complexes derived from mono-nitronaphthalene and nitroanthracene systems. Preprints of papers covering the studies of I and II are available.

How can you possibly absent yourself from Chicago winters?

Best regards,

Claibourne E. Griffin

\[ \Delta \delta (p.p.m.) \]

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H-3</td>
<td>+0.04-0.07</td>
<td>-(0.43-0.67)</td>
</tr>
<tr>
<td>H-5</td>
<td>+1.26-1.40</td>
<td>+(0.55-0.64)</td>
</tr>
<tr>
<td>H-6</td>
<td>+2.50-2.57</td>
<td>----</td>
</tr>
<tr>
<td>H-6.7</td>
<td>----</td>
<td>+(0.53-0.66)</td>
</tr>
<tr>
<td>H-8</td>
<td>----</td>
<td>-(0.32-0.45)</td>
</tr>
</tbody>
</table>

\( R, R' = -\text{CH}_3, -\text{C}_2\text{H}_5 \)


**R. Foster, C. A. Fyfe, P. H. Emslie and M. I. Foreman, Tetrahedron, 23, 227 (1967).*

4 July, 1967

Professor Bernard L. Shapiro,
Department of Chemistry,
University of Illinois,
Chicago 60616, U.S.A.

Ring Currents in Benzene Isomers

Dear Barry,

Sorry for the long delay but Fate has not been very kind to us of late. Our principal vicissitude is that one of our magnet cooling coils became blocked up about 6 months ago and after trying unsuccessfully to unclog it, we have had to wait until a replacement cooling coil could be obtained and installed. As you can imagine, this is not a very simple operation in view of our distance from Palo Alto. However, we hope to be on the air again in a month or so. It will be interesting to do a post-mortem on our 6-year old coil to see what it died of.

In the meantime we have been looking at some other things. One of these is the calculation of the ring currents in the two benzene isomers fulvene and 3,4-dimethylenecyclobutene, using the Hall-Hardisson SCF method.

We have included non-neighbour core resonance integrals in our calculations and in both cases, we obtain ring current contributions which are small and paramagnetic. For benzene, the SCF method gave a diamagnetic shift of 2.53 p.p.m. whereas the "experimental" estimate for this ring current shift for benzene is usually taken as 1.55 p.p.m. Hence we have taken the benzene position as the origin for both experimental and theoretical shifts for the benzene isomers but these calculated theoretical values were scaled down in the ratio 1.55/2.53. The results are presented in Table 1.

.../2
Experimental and theoretically calculated chemical shifts for fulvene and dimethylenecyclobutene. (p.p.m. upfield from benzene.)

<table>
<thead>
<tr>
<th>Proton</th>
<th>Experimental</th>
<th>Ring current calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 4</td>
<td>+0.83</td>
<td>+1.69</td>
</tr>
<tr>
<td>2, 3</td>
<td>+1.16</td>
<td>+1.91</td>
</tr>
<tr>
<td>7, 8</td>
<td>+1.49</td>
<td>+1.50</td>
</tr>
<tr>
<td>Dimethylenecyclobutene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 2</td>
<td>+0.43</td>
<td>+1.82</td>
</tr>
<tr>
<td>5, 8</td>
<td>+2.68</td>
<td>+1.60</td>
</tr>
<tr>
<td>6, 7</td>
<td>+2.57</td>
<td>+1.59</td>
</tr>
</tbody>
</table>

The charge distribution in these systems would not be uniform so that there should be some discrepancy, but it would seem that the ring current calculations give a rather poor estimate of the chemical shifts in these hydrocarbons. For example, the correct qualitative order is not even predicted. Probably the only significant rationalization is to say that the ring currents are small and unimportant in these hydrocarbons and so the pattern of chemical shifts is determined by the interplay of other effects. Chemically, these systems are more like conjugated polyolefins than aromatic compounds.

In view of the above we decided to try another approach and regard the double bonds as essentially localized. We used the C=C, C=H and C-H bond anisotropies determined empirically in recent work by Apsimon et al (Tetrahedron; 23, 2339, 2357; 1967). We used revised values of these anisotropies as communicated to us privately by Professor Whalley. The long range effects of these anisotropic groups were summed up for each proton and the results obtained are set out in Table 2. It is convenient to take ethylene as the reference molecule for both experimental and theoretical chemical shifts.
Table 2

Chemical shifts for fulvene and dimethylenecyclobutene as derived from bond anisotropies (p.p.m. downfield from ethylene).

<table>
<thead>
<tr>
<th>Proton</th>
<th>Experimental</th>
<th>Calculated from bond anisotropies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 4</td>
<td>-1.15</td>
<td>-0.71</td>
</tr>
<tr>
<td>2, 3</td>
<td>-0.82</td>
<td>-0.32</td>
</tr>
<tr>
<td>7, 8</td>
<td>-0.49</td>
<td>-0.05</td>
</tr>
<tr>
<td>Dimethylenecyclobutene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 2</td>
<td>-1.55</td>
<td>-0.80</td>
</tr>
<tr>
<td>5, 8</td>
<td>+0.70</td>
<td>-0.24</td>
</tr>
<tr>
<td>6, 7</td>
<td>+0.59</td>
<td>-0.32</td>
</tr>
</tbody>
</table>

The results obtained here, although they still leave something to be desired numerically, are at least qualitatively correct.

I think they probably emphasize that the ring current effect plays very little part in determining the experimental shifts in these compounds.

Best wishes,

Alan J. Jones

Michael L. Heffernan
July 20, 1967

Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Structure of ThO$_2$H$_5$

A number of possible structures have been proposed for thorium peroxide and we have recently completed (i.e., Mr. Robert Benson has completed) a wide-line study which helps to eliminate many possibilities. We found a rigid-lattice line width of 5 gauss and a second moment of 7.5 gauss$^2$ which eliminates several structures containing water of hydration. The structure we believe most reasonable is Th(OOH)(OH)$_3$ although we still need to complete some calculations to be certain.

Hydrogen Bonding in Hindered Alcohols

Our studies of hydrogen bonding in highly hindered alcohols has been continuing and we have branched out also into intramolecular bonding with double and triple bonds. Recently we have put together some precision dielectric constant and index of refraction apparatus and hope to zero in with these and the nmr and ir on the structures of the dimers (i.e. linear or cyclic). Hope to have something to report soon.

Review of Hydrogen Bonding by NMR

My associate Dr. K.K. Deb and I are completing a review paper on the analysis of hydrogen bonding by nmr methods and we would very much appreciate receiving any up-to-date results that we may have overlooked in the recent literature or that have not yet appeared in print.

Hope you enjoy your California sojourn.

Sincerely yours,

Jeff C. Davis, Jr.
Associate Professor
Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616,
U. S. A.

Dear Barry,

Short Title: Fluorine exchange between PF$_6^-$ and BF$_3$.

We have been looking at the fluorine exchange between tetrabutylammonium hexafluorophosphate and boron trifluoride in CH$_2$Cl$_2$ solution. Exchange rates were determined by comparison of theoretical and experimental spectra. The theoretical spectra were generated by a modification of the computer program kindly supplied to us by Martin Saunders. An example is shown in the following figure.
Comparisons were only made in the $PF_6^-$ resonance region since the $BF_3$ signal was normally too broad and weak to be observed.

It was found that the exchange rate depended upon the concentration of $BF_3$ to the first power and tetrabutylammonium hexafluorophosphate to the one half power. These results may be explained by a simple bimolecular mechanism provided that the salt exists primarily as ion pairs in solution.

\[
(Bu)_4NPF_6 \xrightarrow{\text{fast}} PF_6^- + (Bu)_4N^+ \\
K \approx \frac{[PF_6^-]^2}{[(Bu)_4NPF_6]} \\
\frac{d[(Bu)_4NPF_6]}{dt} = \frac{k}{\sqrt{K}} [PF_6^-] [MF]
\]

where MF is $BF_3$ or $PF_5^-$. There is independant evidence that the salt does exist primarily as ion pairs in these solutions.

The apparent Arrhenius activation energies will not be those of the exchange reactions but will be a measure of the temperature dependance of $\log \frac{k}{\sqrt{K}}$. They are $1.5 \pm 0.2$ kcal. mole$^{-1}$ with $PF_5^-$ and $4.6 \pm 0.2$ kcal. mole$^{-1}$ with $BF_3$.

This work was done in collaboration with Dr. B. Cernicki and Mr. J. Bornais.

Yours truly,

S. Brownstein
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Sometime ago Dr. Bothner-By and I looked at several exocyclic dienes in an effort to determine whether the diene system in a cis arrangement is planar or non-planar. The NMR spectra of the compounds listed in Table 1 were studied over the temperature range +40 to -60°C. It was reasoned that if the diene portion of these compounds was planar or slightly non-planar with a low inversion barrier, the protons (or methyl groups) in the position α to the double bonds would have identical chemical shifts. On the other hand, if the diene portion was non-planar and the inversion barrier high, the groups in the α position would be chemical shifted. This presupposes the ring is either planar or rapidly interconverting between equivalent non-planar forms.

The results were inconclusive in that none of the compounds showed non-equivalence of the α groups except VII. This is not totally unexpected since even if the diene portion is non-planar, a low inversion barrier is quite probable. This is demonstrated by cases III and IV, where one would expect the phenyl ring to be co-planar with the double bond. If this is the case, the inner rings will overlap severely and inversion can occur only if the phenyl ring rotates out of the plane of the double bond or the internal diene angle is much greater than 120°. The fact that the α cyclobutane ring protons are equivalent indicates inversion is occurring rapidly. In VII the fluorenyl groups overlap badly and inversion about the single bond of the diene system can occur only by a twisting of the double bond. This evidently does not happen and the α ring protons remain non-equivalent, even at +160°C. Table 1 summarizes the approximate chemical shifts in these molecules.

We did decoupling experiments on I and II by irradiating the α ring protons. In I the olefinic proton resonances collapse to single lines of ~1.5 cps half-width, indicating that J gem (olefinic) and long range couplings are probably < 0.5 cps. Approximate couplings in II are
Dr. B. L. Shapiro
July 20, 1967

J_{11'} = 2.5 \text{ cps}
J_{12} = J_{1'2} = 0
J_{13} = 1.3 \text{ cps}
J_{1'3} = 1.0 \text{ cps}

This assumes proton 1 resonates at 5.38 and 1' at 5.08 \tau.

Sincerely,

David Koster
Fellow in Independent Research

Title: Exocyclic cis dienes.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shifts ($\tau$) in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure I" /></td>
<td>7.4 (ring) 5.34 (outer); 4.89 (inner) olefinic protons</td>
</tr>
<tr>
<td><img src="image" alt="Structure II" /></td>
<td>8.38, 6.92 ($\beta$ and $\alpha$ ring); 5.38 (outer); 5.08 (inner) olefinic protons</td>
</tr>
<tr>
<td><img src="image" alt="Structure III" /></td>
<td>7.20 (ring) 3.26; 2.86 (aromatic)</td>
</tr>
<tr>
<td><img src="image" alt="Structure IV" /></td>
<td>4.90 (ring) 3.15; 2.70 (aromatic)</td>
</tr>
<tr>
<td><img src="image" alt="Structure V" /></td>
<td>6.96</td>
</tr>
<tr>
<td><img src="image" alt="Structure VI" /></td>
<td>6.85 (CH$_3$) 2.73 (aromatic)</td>
</tr>
<tr>
<td><img src="image" alt="Structure VII" /></td>
<td>3.06, 4.42 (non-equivalent ring protons); 2-3 (aromatic)</td>
</tr>
</tbody>
</table>

\( \phi = \) phenyl \( R = \) fluorenyl (\( \text{fluorenyl} \))
July 20, 1967

Prof. B.L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, 60616  
USA

"Signs of H,F and H,H Coupling Constants in Cyclic Dienones"

Dear Barry:

In continuation of our previous studies1) of proton spin coupling in cross-conjugated cyclohexadienones of type I we now wish to report some results on sign determinations in such systems.

\[ I \]

\[ H \]

\[ O \]

\[ H \]

\[ 6' \]

\[ 2 \]

\[ H \]

\[ 5' \]

\[ 4 \]

\[ H \]

\[ R \]

\[ R' \]

\[ H \]

\[ O \]

\[ H \]

\[ 6' \]

\[ 2 \]

\[ H \]

\[ 5' \]

\[ 4 \]

\[ H \]

\[ R \]

\[ R' \]

\[ H,F \]

\[ H \]

\[ R \]

\[ R' \]

\[ H,F \]

\[ H \]

\[ R \]

\[ R' \]

\[ H,F \]

R = methyl, R' = allyl

Since the "para" proton-proton coupling is very small and unresolvable in normal monosubstituted derivatives of I we have now studied the mono-fluoro compounds II and III in which \( J_{HF}(para) \) is 1.0 and 1.5 Hz respectively and well resolved. These two compounds in principle allow to obtain the relative signs of all H,H and H,F coupling constants by homo- and heteronuclear double resonance. Both the proton (100 MHz) and fluorine (94.1 MHz) spectra were measured which are nearly first order.

Firstly the signs of all six H,F couplings were obtained by proton-proton partial decoupling and tickling experiments. For comparison the \( J_{HH} \) values of I are also given:
<table>
<thead>
<tr>
<th>II*)</th>
<th>III*')</th>
<th>I**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{HF}^{2,3} = +14.2 \text{ Hz}$</td>
<td>$J_{HF}^{2,3} = +15.2 \text{ Hz}$</td>
<td>$</td>
</tr>
<tr>
<td>$J_{HF}^{2,5} = +1.0$</td>
<td>$J_{HF}^{3,6} = +1.5$</td>
<td>$</td>
</tr>
<tr>
<td>$J_{HF}^{2,6} = +7.2$</td>
<td>$J_{HF}^{3,5} = +11.7$</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>J_{HF}^{5,6}</td>
<td>= 9.9$</td>
</tr>
<tr>
<td>$</td>
<td>J_{HF}^{3,6}</td>
<td>= 2.7$</td>
</tr>
<tr>
<td>$</td>
<td>J_{HF}^{5,6}</td>
<td>&lt; 0.3$</td>
</tr>
</tbody>
</table>

*) Measured in 2-molar solution in acetone-$d_6$, $J$ values ±0.1 Hz

**) In $CCl_4$, $J$ values ±0.2 Hz. $CCl_4$ as solvent for II and III does not change the coupling constants significantly.

All $H,F$ couplings are of the same sign and based upon $J_{HF}^{vic}$, positive. It is interesting to note that as the corresponding $J_{HH}^{1}$ in I, $J_{HF}^{2,3} > J_{HF}^{2,6}$. The ratios $J_{HF}^{2,6} / J_{HF}^{2,6}$ in II and I and $J_{HF}^{2,5} / J_{HF}^{2,5}$ in III and I are nearly the same. This seems to indicate equivalent mechanistic routes for the $H,H$ and $H,F$ $^4J$ couplings.

The relative signs of the $H,H$ versus $H,F$ coupling constants may be obtained by heteronuclear $H,F$ tickling experiments which are in progress. We hope to complete this picture soon.

Besides cross-conjugated cyclic dienones we now became interested in linear-conjugated cyclic dienones and their various mono- and dimethyl derivatives. IV and V will be mentioned here as typical examples from a series of seven compounds measured so far.

![Diagram of IV and V](image)
The extent of conjugation in the ground state of these molecules appears to be reflected in both the chemical shifts and the vicinal ($^3J$) and long range ($^4J$, $^5J$ and $^6J$) coupling constants and is supported by $\pi$-electron density calculations. All $J_{HH}$ are of the same (positive) sign in IV as determined both by complete analysis of the four-spin system and double resonance experiments $^3$. In V the long range $J(H, CH_3)$ have alternating signs: $J_{4,CH_3} = -1.6$, $J_{5,CH_3} = +0.4$, $J_{6,CH_3} = -0.6$ Hz.

A detailed discussion of our data on cyclic and open-chain dienones will be published in Helv. Chim. Acta.


2) The preparation of these ortho-dienones by Dr. H. J. Hansen is gratefully acknowledged.

3) IV with $R=CH_3$ has been analyzed by Dr. H. H. Hinrichs, thesis Univ. of Cologne 1966. We thank Dr. H. Günther for this valuable information.

With best wishes,

[Signature]

Prof. W. v. Philipsborn

[Signature]

Walter Regel

Dipl.-Chem. W. Regel
Zur Analyse des Kernresonanzspektrums von 2-Chlorthiophen

Das 60 MHz-Kernresonanzspektrum zeigt für die drei Protonen des Thiophenkerns ein typisches ABC-System, das nach der Näherungsrechnung von CASTELLANO u. WAUGH 1) zunächst behandelt wurde. Die so erhaltenen Parameter wurden für den 1. Teil des Computerrechenprogramm LAOCOON 2) verwendet und damit ein theoretisches Spektrum berechnet. Die Identifizierung und Zuordnung der experimentellen Linien auf die theoretisch berechneten Übergänge war eindeutig. Die folgenden Iterationen im 2. Teil des Programms lieferten nach 6 Teilschritten ein sehr gutes Endergebnis, das durch eine mittlere Abweichung von 0,061 Hz zwischen experimentellen und theoretisch berechneten Linien charakterisiert ist. Tab.1 zeigt die Endparameter der Rechnung. Die Protonenzuordnung entspricht der Fig.1. Tab.2 dokumentiert die numerische Übereinstimmung zwischen experimentellem und theoretisch berechnetem Spektrum. Die Größenordnungen der chemischen Verschiebungen und Kopplungskonstanten entsprechen den Werten, die von anderen Autoren für substituierte Thiophene erhalten wurden. 3) Fig.2 stellt das theoretisch berechnete ABC-System des 2-Chlorthiophen dar.
Tab. 1: Kernresonanzspektroskopische Parameter des 60 MHz-NMR-Spektrums von 2-Chlorthiophen (ohne Lösungsmittel)

<table>
<thead>
<tr>
<th>Parameterart</th>
<th>Chemische Verschiebungen [Hz] *; [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_H^3 )</td>
<td>403,004; 6,7167</td>
</tr>
<tr>
<td>( \nu_H^4 )</td>
<td>398,438; 6,6406</td>
</tr>
<tr>
<td>( \nu_H^5 )</td>
<td>408,104; 6,8017</td>
</tr>
</tbody>
</table>

Kopplungskonstanten [Hz]

| \( J_{34} \) | 3,627 |
| \( J_{35} \) | 1,434 |
| \( J_{45} \) | 5,592 |

Tab. 2: Vergleich der experimentellen und theoretisch berechneten Linien des NMR-Spektrums von 2-Chlorthiophen

<table>
<thead>
<tr>
<th>Linie Nr.</th>
<th>Experimentelle Frequenz [Hz] *</th>
<th>Berechnete Frequenz [Hz] *</th>
<th>Berechnete Frequenzabweichung [Hz]</th>
<th>Intensität [rel]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>391,557</td>
<td>0,012</td>
<td>---------------------------------</td>
<td>0,100</td>
</tr>
<tr>
<td>11</td>
<td>392,710</td>
<td>0,286</td>
<td>0,055</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>396,600</td>
<td>0,747</td>
<td>- 0,033</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>400,560</td>
<td>0,686</td>
<td>0,012</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>401,400</td>
<td>2,410</td>
<td>0,080</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>402,571</td>
<td>0,246</td>
<td>---------------------------------</td>
<td>0,100</td>
</tr>
<tr>
<td>16</td>
<td>402,790</td>
<td>2,697</td>
<td>0,072</td>
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<td>17</td>
<td>404,210</td>
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<tr>
<td>18</td>
<td>405,600</td>
<td>2,029</td>
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Fortsetzung von Tab. 2

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<tr>
<th>Linien Nr.</th>
<th>Experimentelle Frequenz [Hz]*</th>
<th>Berechnete Frequenz [Hz] *</th>
<th>Berechnete Intensität [rel]</th>
<th>Berechnete Frequenzabweichung [Hz]</th>
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<tr>
<td>9</td>
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<td>407,678</td>
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<td>0,002</td>
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<td>5</td>
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<td>- 0,008</td>
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<td>3</td>
<td>412,400</td>
<td>412,453</td>
<td>0,427</td>
<td>- 0,053</td>
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<tr>
<td>8</td>
<td>415,415</td>
<td>415,415</td>
<td>0,021</td>
<td>-</td>
</tr>
</tbody>
</table>

(Fig. 1)

*) downfield von TMS

July 26, 1967

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Professor Shapiro:

The "Average-Energy-Approximation" Conundrum

The energy associated with a second order perturbation may be written

\[ E^{(2)} = \sum_{n \neq 0} \langle 0 | K^{(1)} | n \rangle \langle n | K^{(1)} | 0 \rangle / (E_0 - E_n) \]  

(1)

\[ \equiv \frac{1}{\Delta} \sum_{n \neq 0} \langle 0 | K^{(1)} | n \rangle \langle n | K^{(1)} | 0 \rangle \]  

(2)

Equation (2) defines \( \Delta \), that is known (somewhat incorrectly) as the "average-energy".

For any complete set

\[ \sum_{n=0} \langle n | n \rangle = 1 \]  

(3)

therefore, \( E^{(2)} = \frac{1}{\Delta} \sum_{n \neq 0} \langle 0 | K^{(1)} | n \rangle^2 \} \)  

(4)

It follows from equation (2) that \( \Delta \) is positive for any Hermitian operator \( K^{(1)} \). In addition, if the basis set of functions \( | n \rangle \) belong to a simple system, upper and lower bounds for \( \Delta \) are usually easily established.

For example for a discrete hydrogen atom, \( \Delta \) necessarily lies between 1 and 3/4 of a Rydberg (from the Lyman series).

In magnetic problems we are only interested in a part of \( E^{(2)} \), for which the operator may be divided into two parts, the form of which in standard text books; Eq. (4) becomes

\[ E^{(2)}_{\text{(part)}} = \frac{1}{\Delta} \left[ \langle 0 | K_{a} K_{b} | 0 \rangle - \langle 0 | K_{b} | 0 \rangle \langle 0 | K_{a} | 0 \rangle \right] \]  

(5)

where \( \Delta \) is no longer numerically the same as in equation (4) and may have any positive or negative value.
We would normally expect $\Delta$ to vary from system to system, but it is not known by how much. Cawley and Lauterbur\(^1,2\) have attempted to shed some light on this problem by calculating the energy denominators associated with the $^{19}$F shielding in the crystalline alkali-metal fluorides. This was done by calculating the term in brackets (Eq. 5) and dividing it into the "experimental" paramagnetic shielding. The crystals were described by the Löwdin expansion in terms of Hartree-Fock free-ion wave functions.\(^1,2\)

The denominator ($\Delta$) was found to vary from 17.3 eV for LiF to 4.3 eV for CsF.\(^1\) The latter work also contains evidence that suggests a considerable change in $\Delta$ with pressure.

It is sufficient to say that changes in $\Delta$ may be considerable among related compounds and that assumptions to the effect that $\Delta$ is independent of changes in chemical or physical environment may lead to a loss of significant chemical information, for example, predictions about electron density, bond angles, bond orders, etc., can be erroneous.

In addition to the changes in $\Delta$, as one goes from system to system, there is also the problem that $\Delta$ depends on the nature of the approximate ground state used. Until these changes in $\Delta$ are more fully understood, the average-energy-approximation will remain on shaky footing.

Some of the points raised, suggestions made, and ideas involved above have been discussed in the published work of Unsöld, Karplus, McLaughlan, Saika and others, whose work is hereby acknowledged.

Sincerely,

\[ \text{\textit{La\textit{w}ley}} \]

Seán Cawley

---

\(^1\) Seán Cawley and P. C. Lauterbur, IITNN, 103-8.

\(^2\) Seán Cawley and P. C. Lauterbur, (publication in preparation).
LONG RANGE COUPLING INVOLVING EXOCYCLIC GROUPS

Dear Barry,

The attached table gives some additional values for allylic coupling constants involving exocyclic groups. It can be seen that the data support our previous hypothesis. We have also been able to find similar data for some 3-membered rings, 4-membered rings and 5-membered rings fused to larger alicyclic rings.

It can also be seen that substituent dependence is not very marked and is similar to that in 1-haloalkanes. Some homoallylic coupling constants involving the ethylidene groups indicate that $J_{\text{trans}}$ is generally larger.

The following rationalizations occur to us to account for the apparently general phenomenon of $J_{\text{allylic trans}}$ being larger (i.e. presumably more negative) than $J_{\text{allylic cis}}$ for allylic coupling involving exocyclic vinylic protons:

(a) Barfield predicted, and numerous experimental results confirm that coupling constants across four single bonds may be zero or negative in certain configurations. However Barfield's curves do not, in fact, account for the effect, the values for the indirect contribution to the transoid case being always to the positive side of those for the cisoid case.

(b) One could postulate a direct, positive contribution, larger...
for the cisoid case (closer spatially), thus resulting in a smaller (negative) allylic coupling. However, it is thought that the direct contribution is negative in cases where it is important.

(c) The π effect is not, after all, equal for the cisoid and transoid cases.

With best regards, yours sincerely

G.P. Newsoroff
(S. Sternhell)


<table>
<thead>
<tr>
<th>Structure</th>
<th>J allylic (c/s)</th>
</tr>
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<tr>
<td><img src="image4.png" alt="Structure" /></td>
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</tbody>
</table>
Dear Dr. Shapiro:

Lone pair repulsion in cyclic hydrazines is usually reduced by a pyramidal configuration of at least one of the nitrogen atoms in the ground state. Nitrogen inversion has been found to be slow in some of these ring systems\(^1\)); one of the reasons for this is the increase of lone pair interaction in the transition state.

The spectrum of the diazetidinone 1 in CHBr\(_3\) at +4\(^\circ\)C shows, in addition to a multiplet for the aromatic protons,
a) a methylene group as an AB system at \(\tau = 5.42\) and 6.12 (\(J = 15.2\) cps), coalescing at +67\(^\circ\)C (\(\Delta G^\ddagger_c = 16.7 \pm 0.2\) kcal mole\(^{-1}\)),
b) another methylene group as an AB system at \(\tau = 6.56\) and 6.74 (\(J = 13.7\) cps), coalescing at +59\(^\circ\)C (\(\Delta G^\ddagger_c = 16.6 \pm 0.3\) kcal mole\(^{-1}\)), and
c) two methyl signals at $\tau = 7.66$ and 7.70, coalescing at +32°C 
($\Delta G'_{c} = 16.8 \pm 0.4$ kcal mole$^{-1}$).

At +100°C absorptions a), b), and c) become singlets.

The $\Delta G'_{c}$ values in 2 (13.8 kcal mole$^{-1}$, -6.5°C, acetone-d$_6$) and 
in some other N,N'-diaryl substituted diazetidinones$^2$) are lower 
than in the dibenzyl compound 1. This observation is consistent 
with the nitrogen inversion mechanism, as the comparison of the 
barrier in N-phenylaziridine with that in N-benzylaziridine shows 
the same trend$^3$). We assume inversion at the amide nitrogen is 
faster than at N-1, i.e. N-1 inversion (see formulae) is the pro­
cess measured by NMR. Interconversion of non-planar ring conforma­
tions could represent an alternative explanation for our spectra.
However, this motion of four-membered ring systems$^4$) seems to be 
much faster than the process observed for diazetidinones, the rate 
of which, on the other hand, is consistent with the known facts$^1$) 
on nitrogen inversion.

These results were obtained in collaboration with Professor 
E. Fahr, Würzburg, and Mrs. G. Rissmann, Heidelberg.

Sincerely yours,

Albrecht Mannschreck

1) J.E. Anderson and J.M. Lehnl, J. Am. Chem. Soc. 89, 81 (1967); 
E.L. Allred, C.L. Anderson, R.L. Miller, and A.L. Johnson, Tetra­
Staab, Tetrahedron Letters 1967, 709; J.P. Kintzinger, J.M. Lehn, 

2) E. Fahr, W. Fischer, A. Jung, L. Sauer, and A. Mannschreck, Tetra­

3) A.T. Bottini and J.D. Roberts, J. Am. Chem. Soc. 80, 5203 (1958); 

July 26, 1967

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry,

I am sorry that you had to send me a reminder for my contribution. Our work was interrupted in the middle of May and is now returning to its normal routine.

\[
\text{CrO}_4^- - \text{Cr}_2\text{O}_7^- \quad \text{exchange.}
\]

The kinetics of the \(\text{CrO}_4^- - \text{Cr}_2\text{O}_7^-\) system was studied by \(^{17}\text{O}\) nmr (Figgis et al., Can. J. Chem. 43, 145 (1965); Jackson & Taube, J. Phys. Chem. 69, 1844 (1965)). We are investigating this system using \(^{53}\text{Cr}\) resonances, \(^{53}\text{Cr} (I = 3/2)\) sensitivity (relative to \(^1\text{H}\)) is about \(10^{-4}\). Its resonances in \(\text{CrO}_4^-\) are narrow (less than 20 cps) and observable down to about 2M whereas the \(\text{Cr}_2\text{O}_7^-\) was not observed - presumably due to quadrupolar broadening. A plot of the excess width of the \(\text{CrO}_4^-\) in mixtures with \(\text{Cr}_2\text{O}_7^-\) (slow exchange approximation) vs. the \(\text{Cr}_2\text{O}_7^-\) concentration gives reasonably straight lines with slopes corresponding to a rate constant of \(10^3\) sec\(^{-1}\) M\(^{-1}\). This result agrees with previous measurements. The difficulty however is that the intercepts of the lines vary for each total concentration of \(\text{CrO}_4^-\). This is so because the equilibrium constants for the system are not known for these high concentrations.

In order to measure the \(^{53}\text{Cr}\) resonances in low concentrations (and for other nuclei such as \(^{95}\text{Mo}\) as well) we are working on the incooperation of the c-1024 into the DP system. We shall use the Flux Stabilizer for stability and a specially constructed slow sweep generator. The modulation frequency is 80–200 cps (larger than the linewidth). We hope to report on the performance of this system soon.

Sincerely Yours

A. Loewenstein
A. Loewenstein Y. Egozi
ON THE QUESTION OF 7-SYN- AND 7-ANTI- PROTON ABSORPTIONS IN THE N.M.R. SPECTRA OF NORBORNENES

Analysis of the n.m.r. spectrum of norbornene (I) has been a subject of interest in recent years. The 7-syn- (H₇ₛ), 7-anti- (H₇ₐ), 5,6-endo- (H₅ₙ, H₆ₙ), and 5,6-exo- (H₅ₓ, H₆ₓ) protons all absorb over a relatively narrow spectral range. Whereas the assignment of H₅ₙ, H₆ₙ, and H₅ₓ, H₆ₓ absorption patterns is now well-established, the corresponding assignment of H₇ₛ and H₇ₐ has been a source of some consternation.

Recently, Franzus and his coworkers have resolved this problem via spin decoupling experiments on exo,exo-5,6-dideuterionorbornene; their conclusion that H₇ₐ absorbed at higher field than H₇ₛ. It was our feeling that an unequivocal answer to this question could be obtained via an examination of the n.m.r. spectrum of a 7-monodeuterionorbornene. Accordingly, we have stereospecifically synthesized anti-7-deuterionorbornene (II); a portion of the 100 MHz n.m.r. spectrum of this compound is presented here, along with the corresponding spectrum of the parent norbornene for comparison. Cursory inspection reveals that Tori's reassignment, confirmed by Franzus and coworkers, is indeed the correct interpretation.

In addition, we have extended our studies to include isodrin (III) and aldrin (IV), which may be regarded as substituted norbornenes. The AB spin pattern generated by H₁₀ₛ, H₁₀ₐ in III and IV has been reproduced here. Assignment of these protons was made on the basis of a previously-observed, stereospecific, long-range spin-spin coupling between H₇ₕ and H₆ₕ (vinyl proton) in norbornene. The spectra resulting from the appropriate spin decoupling experiments (H₂-H₁₀ₐ) in III and in IV are shown directly above the normal spectra in each case. Especially striking is the conclusion that the relative absorption positions of H₁₀ₛ and H₁₀ₐ is reversed in these compounds.

A detailed analysis of the n.m.r. spectrum of anti-7-deuterionorbornene, of the vinyl proton-decoupled AB pattern of H₁₀ₛ and H₁₀ₐ in III and in IV, and of the n.m.r. spectra of several other substituted norbornenes will be presented in a forthcoming publication.

We wish to express our sincere appreciation to Dr. LeRoy F. Johnson and to Varian Associates, who kindly obtained the 100 MHz n.m.r. spectra of compounds I and II.

Sincerely yours,

Alan P. Marchand
Assistant Professor of Chemistry

LITERATURE CITED


Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616.

27 July, 1967

Dear Dr. Shapiro,

We have reported on some of our work on p.m.r. spectra of aromatic amines and the derived amides (1ITNMRN 76, 2). Our results were summarised in terms of the acylation shift of aromatic protons i.e. the downfield shift of a given proton when the nitrogen is acylated. One of the most striking features of our results, which has also been observed by others (1ITNMRN 88, 6), is the large shift of H-6 when the 2-position is occupied by a substituent which can hydrogen bond with the amide N-H proton. We rationalize this in terms of a preferred near-planar configuration I.

If the hydrogen bond really plays such an important part in determining configuration it should be possible to alter the acylation shifts by working in more polar solvents where the ortho substituent and the solvent molecules would compete for the hydrogen bonding role. My most recent results show that this can be observed, the H-6 acylation shift falling off as the solvent polarity rises i.e. as the restraining intramolecular hydrogen bond becomes less important. For comparison, H-6 acylation shifts in CDCl₃ and DMSO are shown for a number of 2-substituents (Hz in a 60 MHz spectrum): Br Cl OR NO₂ COOMe

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<th>CDCl₃</th>
<th>DMSO</th>
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<tr>
<td>Br</td>
<td>91</td>
<td>46</td>
</tr>
<tr>
<td>Cl</td>
<td>102</td>
<td>62</td>
</tr>
<tr>
<td>OR</td>
<td>107</td>
<td>86</td>
</tr>
<tr>
<td>NO₂</td>
<td>114-132</td>
<td>36-54</td>
</tr>
<tr>
<td>COOMe</td>
<td>125</td>
<td>85-103</td>
</tr>
</tbody>
</table>

The results can be interpreted in terms of geometry and intrinsic "strength" of the hydrogen bond, and this I will attempt in a paper now in preparation.

(a) this line obtained in conjunction with Drs. S. Sternhell and R.F.C. Brown, and Mr. L. Radom.

Yours sincerely,

[Ian D. Rae]
Dr. Barry L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry,

In our letter dated February 24, 1967 we described a method of converting the A60 field sweep decoupler to frequency sweep. We would now like to report some changes in the setup and some ideas concerning the use of the NMR Specialties HD60A heteronuclear decoupler.

Calibrated Frequency Sweep Double Resonance with the Varian A60

We have modified our V6058A and our A60 as per the following diagrams to allow frequency sweep spectra to be presented on the A60 flat bed recorder and on precalibrated chart paper.

The components were contained in a rack mounted box and connected to the A60 and the hp 3300A Function Generator by means of shielded cables. The decoupler was modified so that it could be switched from field sweep to frequency sweep with a relay.

To use the instrument, the decoupler is set on phase lock and the unit is placed in frequency sweep mode. The protons to be irradiated are brought into resonance with the field offset control and the A60 offset control. (The range of the field offset control is set by the A60 sweep width switch.) The desired frequency sweep width is selected and the decoupler is put in the decouple mode. The protons to be observed are brought into resonance using the frequency offset control. The decoupled spectrum is then presented on the A60 recorder. The decoupling field position may be optimized using the field offset control.

The new arrangement enhances the utility of the decoupler in tickling and nuclear Overhauser experiments as well as in decoupling experiments. However, we have found one serious problem which apparently arises from some unknown deficiency in the decoupler. In the decouple mode, a sixty cycle hum modulates the field via the decoupler. The modulation index increases with increasing $H_2$ and becomes pronounced at the power levels necessary for decoupling. We have found that the modification neither increases nor decreases this undesirable modulation. Any solution to this problem would be welcomed.

Simplified Deuterium Decoupling

During the course of other work we found it necessary to frequently run deuterium decoupling experiments. We have an NMR Specialties HD60A decoupler and a modified room temperature probe. However, we wished to do variable temperature work and did not wish to risk loss of resolution and sensitivity arising from the probe modification. We have found that a black box (circuit given below) inserted between the sample probe and the sample receiver allows us to inject a 9 Mcps r.f. signal into the probe with sufficient power to decouple DMSO-$d_5$ to a single peak.
(w 1/2 = 0.25 cps) with no loss in resolution and with no more than 10% loss in sensitivity. No attempt was made to double tune the probe.

**Black Box Diagram**

The A60 is used to align the box and the HD60A. The spectrometer is peaked up on the water resonance (H₂O = 0.05 mg) and then the box is inserted. The 60 Mcps filter is tuned to give a maximum signal at the recorder. The water sample is then removed. The HD60A carrier null is set at off null and audio power (at a frequency near that required for decoupling) is applied to the decoupler. The 9 Mcps filter is then tuned for a minimum at the signal level meter. The carrier and the other side band are nulled to a minimum at the signal level meter. When all adjustments are complete, the meter should read less than 5 with the spectrum amplitude at 100, the r.f. field at 0.05 mg and the decoupler audio gain at 30.

We have found that in normal operation the magnetic field drifts enough so that frequent resetting of the decoupling frequency is necessary. We have circumvented this problem by running the spectrum in phase lock mode. The magnetic field is then locked to a crystal oscillator, resulting in a stable magnetic field and simplified operation of the HD60A.

Sincerely,

Edgar Garbisch

Richard Sprecher
Block Diagram

```
Frequency Sweep Unit

V6058A decoupler

hp3300A

A60
```

Frequency Sweep Unit

- 12k - 10W
- Sweep Width Cal.
- Ramp Voltage
- 50Ω
- Field Offset
- 50Ω - 1 turn
- Frequency Offset

Resistors 17% wire wound

1Ω to 3300A

1Ω to 3300A

1Ω to 3300A

Terminal Strip

BPDT Switch

To 3300A

Freq. Control

To decoupler relay
A60 Modification

Cable detail

Frequency sweep unit

A60
V6058A Modification

Chassis Changes

- VFO Calibration
- 6.3V DPDT Relay
- J2118 L
- J2117A
- NO
- NC
- J2111A
- NO
- NC

To BNC
Front Panel
J2119 - F
L M N R
R wire previously connected to R

6.3V common
-6.3V
Jack on rear panel

Resistor Card Additions

- 500
- 150
- 200Ω
- 20 Turns

Note: Set VFO Level Adjust so that the voltage at J2117A is the same on either field or frequency sweep with HP3300A set at 5Kc and maximum voltage.
Prof. Barry Shapiro  
Dept. of Chemistry  
Illinois 2 Technology  
Chicago, Illinois 60616

Dear Barry:

We have a couple of items which we think are of general interest.

Modification of the HA-100 Offset Circuitry for Sulfuric Acid Lock.  
We have found it convenient for most samples to use sulfuric acid as a lock in the HA-100 spectrometer. The best results have been obtained by using a capillary containing Reagent Grade concentrated sulfuric acid, (resonance at approximately $\tau = -1.6$ ppm.) together with TMS dissolved in the sample for the internal reference. With the standard HA-100 the offset range is not adequate to lock on to concentrated sulfuric acid while adjusting the TMS resonance to be at the right-hand edge of the spectrum. We have achieved an additional 500 Hz offset by inserting a one-thousand ohm variable resistor in series with the resistor used to control the 2500 Hz fixed offset. The variable resistor is adjusted to give the desired additional offset. A throw switch is included so that the added resistance can be switched in or out of the offset circuit.

This arrangement has several advantages particularly when recording 100 MHz spectra. First, distortions from the lock signal are minimized in the spectral region. Perhaps even more important, the integral in the usual spectral region does not have an additional contribution from the lock signal. There are obvious advantages in using this set-up with a time averaging computer. We have had occasional trouble from spinning sidebands caused by the presence of the capillary which can usually be minimized by adjustment of the spinning rate. Included is a 100 MHz spectrum of 100 $\mu$g of crotonaldehyde to show the sort of spectrum that one gets from this arrangement. In this case we used the microcell suggested by Lundin (IIT NMR 28, 21) and our averaging computer for 13 sums (~1 hr.).
Computer Program. We (Roger Reavill) have adapted Axel Bothner-By's LAOCN3 program for our 360/65 computer. He will be happy to send a listing of this program to other 360 users.

Best wishes.

Yours very truly,

THE PROCTER & GAMBLE COMPANY
Research & Development Department
Magnetic Resonance Section

T. J. Flautt
K. D. Lawson
J. E. Haynes
L. V. Haynes
R. E. Reavill
O.1 MG. CROTONALDEHYDE
I3 C.A.T. SPECTRUM
SCAN RATE = 4 Hz/SEC
SOLVENT = CCl₄ + 0.1% TMS
CONC. H₂SO₄ LOCK
FREQ. RESPONSE = 2 Hz
July 27, 1967

Dr. Bernard L. Shapiro  
Department of Chemistry  
Stanford University  
Stanford, California 94305

Dear Barry,

This is another request for "publishing" an inquiry, this time on

**Adaptation of Computer Programs to IBM-360's.**

We will have our IBM-360 operational in the very near future and plan to use it for the computation and plotting of NMR spectra, among other things. The computer is a model 30 (65 K), but will be a model 40 (265 K) early next year, and has Extended DOS.

I should appreciate hearing from anyone having experience with running the Swalen/Reilly and the Castellano/Bothner-By programs on this type of computer, especially with regard to problems related to software.

Best wishes for a pleasant and fruitful year at Stanford.

Sincerely yours,

Ernest Lustig  
Division of Food Chemistry  
Bureau of Science - S-410
nr: ITT NMR Newsletter

Title: Carbonium Ions 3.

Dear Dr. Shapiro,

In one of our preceding contributions to this Newsletter we gave some NMR data about aryl cyclopropyl carbonium ions. The spectra of these ions showed that the ortho-protons in the ions are non equivalent. The conclusion one might draw at first sight, however, that this non equivalency is caused by a spatial preferred position of the threemembered ring, is not justified by further experiments.

The spectra of three anisyl alkyl carbonium ions are given in Figs 1-4. In the anisyl dimethyl ion (Fig 2) both ortho protons are obviously equivalent. The aryl part of the spectrum shows the normal $A^2(A_2B_2)$ pattern.

When, as in the anisyl monomethyl ion, however, the alkyl groups are different, an analogous non equivalency as in the cyclopropyl containing ions, is encountered (Figs 3 and 4). Here the aryl parts of the spectra are complicated by the fact that the signals due to the $\alpha$-protons are found in the same regions. The quartet ($\pi$) of the $\alpha$-protons in the anisyl methyl ion is position at about 8.8 p.p.m. from TMS; the doublet (o) in the cyclopropyl ion at about 8.4 p.p.m. This interpretation is confirmed by the 100 MHz spectra (Fig. 1) and by double resonance experiments.

The corresponding benzyl- and tolyl carbonium ions are much less stable, the cyclopropyl substituted ions being exceptions. This is further evidence for the stabilizing influence of threemembered rings in carbonium ions.

The $\alpha$-methoxyl group is strongly electron donating by resonance and hence stabilizes the ions:

$$\text{CH}_3\text{O} + \text{C} \rightarrow \text{CH}_3\text{O}^+ \text{C}$$
The NMR spectra are an indication that in the ions a plane conformation is preferred. The anisyl methyl- and anisyl cyclopropyl ions were prepared from the parent alcohols, the anisyl dimethyl ion from the α,α-methyl anisyl ethene, at -60°C in HSO₃F-SO₂.

At this point we should also like to reply shortly to the remarks made by Dr. Olah on our work. We think that the differences between the spectrum of Olah and ours, ascribed to the phenyl cyclopropyl carbonium ion, are not due to the use of different standards, to medium effects or to the influence (temperature dependence) of the spectrum:

i) We compared several spectra of members of this group of ions measured in various mixtures of HSO₃F-SbF₅-SO₂ (the ratio HSO₃F-SbF₅ varying from 4:1 to 10:1) and in HSO₃F-SO₂ and hardly noticed significant differences in chemical shifts;

ii) Exchange of the exo-cyclic C-H proton has never been observed in experiments with these ions. It is our experience that neither (extreme) acidity nor lower temperature are decisive for the observation of the signals due to these protons;

iii) We have recorded the NMR spectrum of a freshly prepared solution of the phenyl cyclopropyl ion at -80°C and also recorded the spectrum after decomposition had taken place. The former spectrum is identical to our spectrum as published, the latter closely resembles the one given by Olah.

Yours sincerely,

(Th. J. Sekuur.)
(P. Kranenburg)
(G.J. v. Kampanhout)
August 4, 1967

Dr. Bernard L. Shapire
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

"Hindered Rotation of a CFBr₂F Substituent. A Possible Nonbonded Br-F Coupling?"

We have used ¹⁹F nmr to study the stereochemistry of the products of free-radical addition of CFBr₃ to norbornene derivatives, such as the Diels-Alder adduct of maleic anhydride and cyclopentadiene, I. Although norbornene itself gives almost exclusively trans addition of CFBr₃, the presence of a bulky endo substituent, such as the anhydride carbonyl groups of I, greatly increases the proportion of exo, cis product, in the above case adduct II. The principal evidence for the structure of II comes from the temperature dependence of its ¹⁹F spectrum. At -50° three conformers are observable for II with chemical shifts (expressed as ppm upfield from CFBr₃) of 37.7 (doublet, J₁₉,H,F = 13.5 cps), 55.5 (singlet, J₁₉,F = 0) and 67.3 (doublet, J₁₉,F = 33.5). The three peaks for II coalesce near 50° to a single broad peak. Adduct III shows only a single doublet near 64.3 ppm (J, approximately 25 cps) at all accessible temperatures. These observations are best accommodated by the suggestion that rotation about the bond joining the CFBr₂ group to the ring is severely inhibited by the cis bromo substituent in II.

An interesting further observation notes that heating of II above 50° brings the expected sharpening of the single broad ¹⁹F peak until temperatures of ca.
160° are reached. Further heating to 200° gives an essentially unchanging peak width of about 60 cps. An interesting long-shot explanation for the failure to observe further narrowing of the broad peak would involve nonbonded coupling of the fluorine to the cis vicinal bromine atom, which becomes observable at the higher temperatures as quadrupolar relaxation of the 79Br and 81Br nuclear spins becomes less efficient.

Yours,

Adriane Gurak

J. C. Martin
To
Dr. B. L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Non observable $^4J$-long range Coupling of Bicyclo[3.1.0]hexenols

Dear Dr. Shapiro,

Recently we have synthesized 2,6-diethyl-3,4-diphenyl-bicyclo[3.1.0]hexene(2)-ol-(1) by reduction of the corresponding ketone with lithium-aluminum-hydrid(1,2). This reaction yields two products which are stereoisomers. We tried to find out the correct stereo-chemistry by NMR, because this two compounds have a different spatial arrangement of the tertiary protons ($H_A$ and $H_A'$).

In B a W-shaped geometry (3,4) of $H_A'$ and $H_B$ is possible which should give rise to $^4J$-long range coupling, whereas in A this coupling should be lacking.
When degassed samples of $A$ and $B$ were investigated by NMR the following data were obtained (5):

$A$: (CDCl$_3$) $\delta$ (ppm): 0.8-1.5 (10 H, CH$_3$-), 2.32 (H, CH$_2$-), 5.18 (1 H, -CH), 7.15 and 7.21 (10 H, C$_6$H$_5$-) ppm.

$B$: (CDCl$_3$) $\delta$ (ppm): 1.03; 1.17 (6 H, CH$_3$-), 1.61 (2 H, cyclopropane-protons), 2.41 (2 H, CH$_2$-), 4.74 (1 H, -CH), 7.17 and 7.24 (10 H, C$_6$H$_5$) ppm.

A comparison of the tertiary proton signals ($A$: 5.18 ppm, $B$: 4.74 ppm) showed that the expected fine structure (a doublet for the methine proton in $B$) was completely lacking in both spectra. These methine signals could not be resolved but a scale expansion to the sweep width of 50 cps led to different line shapes of the signals concerned. $A$ had a line width at half height for the -CH-proton of 2.7 cps whereas $B$ had a line width of 4.4 cps. This broader signal must involve a $J$-coupling in the order of 1 cps, therefore we assign structure $B$ to the exo-2,6-diethyl-3,4-diphenyl-bicyclo[3.1.0]hexenol and structure $A$ to the endo-form.

From the cyclopropane-protons $H_B$ and $H_C$ no further information could be obtained.

This findings are somewhat surprising since v. Philipsborn (6) was able to detect a long range coupling of 0.9 cps in the molecule $C$. At the moment we are studying other bicyclo[3.1.0]hexenols in this direction.

Yours sincerely

(Doctor Heinz Dürren)

Literature

5) All spectra were recorded with a Varian A 60 spectrometer.
6) W. v. Philipsborn, lecture held at the 5th NMR Workshop, Zürich, 1965.
Decomposition of Unresolved Multiplets

Dear Barry,

For some time we have been interested in the problem of generating "differential" double resonance spectra, where all resonances are cancelled except for those perturbed by the irradiation. Experimentally this entails pulse modulation of $H_2$ at a very low frequency, and inversion of the signal in synchronism with the pulses, either in a conventional lock-in detector or through the "add" and "subtract" functions of a time averaging computer. Although this proved to be straightforward for heteronuclear double resonance, our first attempts at proton-proton work could only be described in terms of a phenomenon first reported by Thurber's grandmother, i.e. "modulation was leaking out all over the molecule." Every transition appeared to be directly connected to every other. We feel this was due to the rapid transients induced in the internal lock field-frequency loop as $H_2$ was switched, displacing all the spectral lines. It can be cured by introducing a short blanking period during which both the "add" and "subtract" functions are inhibited:

Among the several possible applications we would like to describe the decomposition of an unresolved multiplet--a 0.05 Hz doublet in the spectrum of 3-bromothiophene-2-aldehyde due to long-range coupling between the proton at position 4 and the aldehyde proton. This doublet consists of transitions $X_1$ and $X_2$, distinguishable by the different ways in which they fit into the energy level diagram; $X_1$ is connected to $M_1$ while $X_2$ is connected to $M_3$. Thus weak irradiation of line $M_1$ causes $X_1$ to split into a doublet but leaves $X_2$ unaffected. Pulse modulation of the irradiating field on $M_1$, followed by synchronous detection of the signal results in a response with a central

Electricity was leaking all over the house.
positive peak (X1) flanked by two weaker, negative signals (X1 split and inverted) with negligible contributions from X2.

Our time averaging device was a Mnemotron CAT 400 which has the feature that signals in alternate channels may be steered into two quite separate regions of the memory (let us call them the odd and even locations). At read-out, first all the odd channels are displayed sequentially and then, starting again at the left-hand edge of the recorder, the even channels. We therefore alternately irradiated lines M1 and M3, storing the X1 response in the odd locations and the X2 response in the even locations. The resulting trace is shown in the Figure.

![Graph showing X1 and X2 responses](image)

Transient nutations of the magnetization vectors persist for a considerable time after H2 is switched. It should be pointed out that there are certain features about these transient effects that are incompletely understood—in particular, oscillatory signals could be detected at a frequency that appeared to depend on the levels of both H1 and H2. Unless the pulse period was increased sufficiently (22 secs) to minimize such transient effects, there was a detectable amount of "cross-modulation" between the X1 and X2 responses.

Yours sincerely,

Ray Freeman

Bo Gestblom

---

3. Varian Postdoctoral Fellow, on leave from the Institute of Physics, Uppsala.
SUBJECT: AUTOMATIC ANALYSIS OF NMR SPECTRA

July 26, 1967

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Dear Barry:

Thank you for the reminder. Some time ago (IITNMR 97,52) I mentioned that I was writing a program which consolidated NMREN and NMRIT with DECOMP and ASSIGN so that chemical shifts and coupling constants could be automatically determined directly from the digital spectrum. The philosophy of the program was described in the above mentioned newsletter. Although the program is not complete, I have obtained enough data from it to allow estimation of the times likely to be involved for the automatic analysis of 3 and 4 spin systems. Due to lack of facilities to obtain digital spectra, all spectra except one A₂B₂ spectrum, have been obtained by calculating the data points from the sum of Lorentz lines obtained by using literature data in NMRIT(0). Previous experience with DECOMP has shown that good experimental spectra can be decomposed in essentially the same time as calculated spectra, so my values should be good estimates of times required for real spectra. Two ABC spectra, acrylonitrile and 2-chlorothiophene, have been run completely through the program, from the digital spectrum to the chemical shifts and coupling constants, in one step. The time required for each calculation was slightly less than 2 minutes on the IBM 7094.

Thus far, the four spin systems A₂B₂ and ABCD have been done in two steps: 1) decomposition and normalization and 2) ASSIGN, NMREN and NMRIT(N). Each step of the A₂B₂ case required slightly less than two minutes while the assignment step of the ABCD case took about four minutes.

Eleven lines were found in the acrylonitrile spectrum and 12 lines in the 2-chlorothiophene spectrum, which allowed all energy levels to be connected. Some of the very small combination lines at the extreme edges of the spectrum were lost because of the threshold setting of the baseline. To indicate how well the decomposition works by itself, the small peak of the following doublet was found during the second trial by DECOMP. On the other hand, very small lines close to large lines may not be resolved as exemplified by the following two examples.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>404.53</td>
<td>1.98</td>
</tr>
<tr>
<td>405.37</td>
<td>.14</td>
</tr>
</tbody>
</table>
Dr. Bernard L. Shapiro

July 26, 1967

The difference between the data points and those calculated for a single peak having an intensity equal to the sum of the two peaks was not large enough for DECOMP to detect the presence of two peaks. However, the peaks would be found if two sets of starting parameters were introduced to DECOMP.

Results to date indicate that it should be possible to automatically analyze a large fraction of three and four spin systems in times ranging from two to less than 10 minutes on a computer equivalent to the IBM 7094. I hope to have the complete program more thoroughly checked out with experimental data before too many months have passed.

Sincerely yours,

T. R. Lusebrink
Senior Research Scientist

TRL/pl
Dear Dr. Shapiro,

1. **Long Range Couplings in Phenalene**

   We have recently analyzed the 100 MHz NMR spectrum of phenalene (I) and found some remarkable long range couplings between the \( \text{CH}_2 \) and various other ring protons.

   \[
   \begin{align*}
   J_{12} &= 4.0 \\
   J_{13} &= 2.1 \\
   J_{14} &= 1.6 \\
   J_{16} &= 1.1 \\
   J_{17} &= 0.7 \\
   J_{19} &= 1.2
   \end{align*}
   \]

   (measured in CDCl\(_3\))

   We thank Professor Prinzbach (University of Lausanne) for giving us the sample.

2. **Temperature dependence of field gradients in alkali halide crystals**

   Some results from the investigations of electric field gradients around substitutional impurities in alkali halide crystals have been reported earlier in IIT-NMR Newsletters (No. 42 and No. 73). In the meantime sensitive double-resonance techniques have been developed to study these field gradients\(^\text{1-3}\). The double-resonance measurements were all performed at liquid nitrogen temperature for experimental convenience. To be able to relate our results obtained at room temperature to the liquid nitrogen results we started an investigation of the temperature dependence of the field gradient.
The resonance investigated is that of the nearest $^{127}$I neighbours to a Rb impurity in a KI crystal. The resonance lines of these nuclei have very large shifts$^4$ and we measured the temperature dependence of the shift (about 300 G at 14 kG) of the central line. We obtained a quadrupole coupling constant $e^2qQ/h$ of 19.7 MHz at 102° K and 17.1 MHz at 392° K. All measured points between these temperatures fall close to a straight line with the slope of $-9.1$ kHz/degree.

The obtained result shows that the temperature dependence is quite large. The field gradient is supposed to be proportional in first order to $r^{-3}$ where $r$ is the distance from the impurity ion. The relative change of field gradient can then be compared with the relative volume change, and we find that the measured values are 4 to 5 times larger than expected. This disagreement may be attributed to the large (not only first order) distortion at the nearest neighbour of the impurity ion, and we cannot make any generalization of this first result except that temperature effects are important.

References:

3. Position available

We are looking for a chemist with PhD in organic or physical chemistry for our Application Laboratory in Zurich. Experience in operation of NMR spectrometers and interpretation of NMR spectra is required. Duties involve technical sales support, some travelling and application research. We are happy to give further information to interested people.

Sincerely yours,

U. Scheidegger, PhD. L.O. Andersson PhD.
Manager

L.O. Andersson PhD.
July 21, 1967

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Scrooge:

Epexegesis

I am immeasurably distressed that I strained your sense of humor past the yield point in my innocent letter of July 5. While writing it, I recalled your plea last spring for some light banter to enliven the increasingly dull and stodgy pages of IIT NMRN, and merely tried to do my bit. If I had known that such advertisements had already driven you nearly distraught, I should have addressed myself to that problem instead. Each of us should do his bit to help with the editorial chores and responsibilities of this communal information service, and I should like to propose the following policy: Letters of solicitation (for post-doctorals, pen-pals, samples, help, etc.) should be classified as advertisements and a charge should be made for each page. Since the complications with bookkeeping, different currencies, and the Internal Revenue Service would appear to preclude cash payments, such a letter might count as minus one month's subscription credit. To demonstrate my seriousness, I not only withdraw the second paragraph of the letter in Issue No. 106, but request that I be docked one month for it. Furthermore, if you should choose not to implement this suggestion, you may apply this letter also to my account as one month's negative credit, to atone for my having wasted your time.

Humbly yours,

Paul C. Lauterbur

Cont'd from page 67

Source of Advertisements, etc.

G. Mavel (Paris)
H. Dreeskamp (Stuttgart)
W. von Philipsborn (Zurich)
R. Hoffman (Uppsala)
A. L. Porte (Glasgow)
P. C. Lauterbur (Stony Brook)

Charge

1 case of Romanee-Conti '47
1 case of Schloss Johannisberger Kabinett '59
a life-size replica of a 23.5 Kgauss magnet, made of Lindt chocolate
almost any Swedish blonde (f.)
a credit card good at St. Andrew's
his weight in Long Island ducklings

I would enjoy hearing from you again, Paul, whenever you need another respite from doing Big Science.

Yours westwardly,

Bernard L. Shapiro
5 August 1967

Dear Northcote,

With the possible exception of the second law of thermodynamics, it is the serious wisdom of your pronouncements which commands my most unquestioned faith. Indeed, I have long counted myself among those to whom a Lauterbur statement, suggestion or opinion carries the same cachet of respectability as pronouncements beginning with "density matrix theory shows" or "Pauling says" or "inclusion of higher order terms reveals". Thus I was poorly pre-conditioned to suspect the remote possibility that you had attempted humor. (In terror for their present careers, Johnny Carson, Mort Sahl and Soupy Sales have just purchased copies of Abragam's book). Thank you, however, for your attempts to relieve the indeed stodgy pages of the Newsletter. That you also find the latter "increasingly dull" is a pity - I would remind you that reading the Newsletter is optional, not mandatory, and you can always let your subscription lapse again if you wish. I hope you will not choose this extreme course of action, since the last time you were axed for non-payment, the Newsletter nearly died, obviously from lack of your managerial nourishment. But enough preamble - on to the content of your most recent, characteristically meaty letter.

Like all great and seemingly simple ideas, your new proposal has several possible extensions. A few of these follow, and I would be pleased to receive your comments, etc.

(1) Are all post-doc ads = -1 month?, or should good ads (mine, those of friends likely to send students to me) be less penalized than bad ads (yours, or the competition's, etc.)?

(2) Should the post-doc ads be handicapped, like golf scores or horse races - e.g. inorganic solid state NMR work at the U. of Greenland = -1 month, whereas at some lush Cambridge, California or Zürich-type location doing Nobel prize quality high resolution work with Mrs. Ponti = -10 months?

(3) Should negative credit be given for other kinds of pseudo-contributions? E.g. - how about -4 months for a description of how to clean out spectrometer cooling coils, -2 months for contributions whose total length exceeds four pages, -11 months for scooping the editor, -3 months for the discovery of a non-equivalent methylene group, -5 months for any contribution which appears in the formal literature within three months, etc., etc.

(4) Similarly, what about +n months credit (n>1) for various especially worthy contributions? I am sure you can make some specific suggestions for such a hierarchy (e.g. +2 months for finding something new for Ray Freeman to modulate, +3 months for getting him to work on a system with more than 3 spins, etc.). Who knows, maybe this will allow one to attempt quantitative editorialization?

(5) Perhaps it might be possible to take yet another approach, and one which will avoid Negative Numbers (which Messrs. Tiers and Shoolery (?) some time ago decided independently were a bit much for most organikers). While cash payments for ads, etc., would be too difficult, perhaps bribery in kind might get around the logistic problems. The following are meant as illustrative examples of how this system might operate - I leave it to you or to others to provide more examples.

Continued
External Referencing ad Nauseam.

We have been interested in measuring the chemical shifts of water protons in aqueous systems. We opted for a spherical external reference system. Actually that turned out lucky because our experience with spherical cells enabled us to make passable spherical microcells (2). We have recently returned, however, to the study of external reference systems. We (3) and others (4) have shown that the substitution method is subject to some error. We have realised that the other conventional methods (coaxial cylindrical cells or a spherical cell inside a cylinder) might also be subject to some error. This would be due to the fact that in both types of system the standard substance does not traverse the same magnetic field as the substance under study, as the cell is spun. Consequently, if there is any field gradient, a chemical shift error might be introduced. To test this we constructed two types of cell in which both samples would traverse the same field. One consisted of four melting point tubes inside a 5mm.O.D. NMR tube; the sample was placed in two tubes and the reference in the other two. The other cell was a double D one, made by putting a glass partition down the centre of a 8.5 mm.O.D. tube. Both cells gave numerous, large spinning sidebands. We have concluded that, at least for proton work, these new types of cell do not offer any practical advantages over coaxial cylinders. Under certain conditions of severe magnetic field gradients, the double D cell does appear to give more accurate results than coaxial cylinders. However, these conditions are such that very broad resonance lines are observed, with the attendant inaccuracies in locating the centre of the peak. In these cases one would not take measurements anyway, but improve the field homogeneity by means of the field correction coils.

G.E.Hall  
D.J.Giechardi  

Colworth House,  
Sharnbrook.  
Bedford.

1. Newsletter No.81  
Frost and Hall Nature 1965, 205, 1309

2. Frost, Hall, Green and Leahe, Chem. & Ind., 1967, 116  
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"Positive Halogen Compounds. VI. Preparation of Alkoxydimethylsulfonium Salts and their Role in the Kornblum Oxidation. Revision of the Structure for the Olefin-Bromotrinitromethane Adduct"  
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"Bacterial Carotenoids. XX. The Carotenoids of Mycobacterium phlei strain Vera. 2. The Structures of the Phlei-xanthophylls. — two Novel Tertiary Glucosides"  
S. Hertzberg and S. L. Jensen  
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K. Torrssell and K. Wahlberg  
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A. A. Khan, S. Rodmar and R. A. Hoffman  
Acta Chem. Scand. 21, 63  (1967)

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"Sulfones and Sulfenes — the S-Oxides and S,S-Dioxides of Thioaldehydes and Thioketones"  
G. Opita  

"A Simple Preparation of Diazocarboxylic Esters from Ethyl Argentodiazoacetate and Alkyl Halides"  
W. Schollkopf and N. Rieber  

"Synthesis of Oxalactams (2-Morpholinones) from Aziridinium Tetrafluoroborates and Hydroxy Esters"  
E. Pfeil and U. Harder  

"Detection of Hydrogen Bridges between Inosine and Other Nucleosides by NMR Spectroscopy"  
K. H. Scheit  

"Synthesis of 1,3-Di-O-acetyl-glycerol from Glycerol and Acetic Anhydride and a Method to Determine the Ratios of 1,2-Di-O-acetyl-glycerol and 1,3-Di-O-acetyl-glycerol in a Mixture"  
L. Holmqvist  
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"Syntheses of L-(-)-Tecostidine and Related Acrichinines"  
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"Proton Magnetic Resonance Spectra of Some Organophosphorus Compounds"  
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"Pigments of Marine Animals. IV. The Anthraquinoid Pigments of the Crinoids, Comatula Pectinata L. and C. Cratera A. E. Clark"  
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"Cyclic Nitrones. I. Reactions of a-Keto Nitrones at Nitromethane"  
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D. A. Mutchinson, L. J. Olsen, and A. M. Sargeson  
Australian J. Chem. 20, 597 (1967)

"Identification of a Plastoquinone and Two Naphthoquinones in Anacystis Nidulans by NMR and Mass Spectroscopy"  
C. F. Allen, N. Franke and O. Kiryussa  

"A Magnetic Resonance Study of the Citrate Synthase Reaction"  
P. A. Sere  

"Compounds of Phenylphosphonic Acid"  

"The Nature of the Intermediate Generated in the Catalysed Aquation of Some pCO[(NH) 2] 2+ ions"  
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"The Chemical Constituents of Australian Eucalyptus Species. III. The Constituents of E. Kunzea Bentham"  
J. A. Dimmen, H. Ritchie, and W. C. Taylor  
Australian J. Chem. 20, 567 (1967)

"Action of Triethylamine on 3,3,3-Trifluoro-2-(Tri-fluoromethyl)propionyl Fluoride"  
I. L. Knunyants, Yu. A. Cheburkov, and Yu. E. Aronov  

"Mobility of Hydrogen Atoms in Mono-o-PolyFluoroalkanes and Related Compounds Communication 1. 2H-Hexafluoro-2-(Trifluoromethyl)Propionyl Fluoride"  
I. L. Knunyants, Yu. A. Cheburkov, and Yu. E. Aronov  

"Bistrifluoromethylketene Communication 7. Structure of the Dimer"  
I. L. Knunyants, Yu. A. Cheburkov, and M. D. Bargemova, E. I. Fedin, and P. V. Petrovskii  

"Identification of a Plastoquinone and Two Naphthoquinones in Anacystis Nidulans by NMR and Mass Spectroscopy"  
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I. L. Knunyants, Yu. A. Cheburkov, and Yu. E. Aronov  
"Fluorine Derivatives of Polyhydric Alcohols III. 1,1,1-
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Atom III. Relation Between Structure and Reactivity in
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"Synthesis of Some Phosphonium Salts and 1,1-Diphenyl-1,
3-Pentadienyl Cobalt Derivatives" I. Prognostic Results for Proton-Proton
Coupling Constants
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"Structure of Busch Eno-thiatriazolines"
M. Otta, H. Kato and T. Kanako

"Hydrocarbons in Patchouli Oil"
H. Tsukui, K. Nishimura and Y. Hirose

"Medium-Sized Cyclophanes. III. The Nitration Reaction of
[2.2]Metacyclophane with Benzoyl Nitrate"
M. Fujimoto, T. Sato and K. Naka

"Proton Magnetic Resonance Spectra of Methyliodothio-
phenes"
K. Takahashi, I. Ito and Y. Matsuki

"Reaction of Triethylaluminium with Electron Donors"
Y. Takeda

"Asymmetric Synthesis with Sugar Derivatives. II.
Asymmetric Syntheses by Methoxy-Mercuration of
Cinnamic Esters of Sugar Derivatives"
M. Kawana and S. Emoto

"Transposition of Ketals in Patchouli Oil"
S. Shimokawa, J. Sohma and M. Itoh

"A Study of Halogen Exchange Reactions Between Methyltin
Halides by N.M.R. Spectroscopy"
H. V. Van den Berghe, G. F. Van der Kelen and Z. Eeckhaut

"NMR Experiments on Ketals IX. 1,3-Dioxanes with Atrial
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"Contributions à l'étude des hétérocycles sulfurés
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chloranthène"
P. Faller

"Un nouvel exemple de couplage "H - H les sels de
pyridanine""
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